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Direct Thermochemical Conversion of Sewage Sludge to Fuel Oil

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16. ABSTRACT

A disposal method for primary sewage sludge and industrial sludges which generates boiler fuel as a product and is energy self sufficient or energy-generating is described. The method involves direct liquefaction in a mild aqueous alkali above 250°C and was demonstrated for about 100 hours in a reactor having a 50 pound per hour capacity. The boiler fuels recovered from the process were in the form of a water insoluble oil, char and gas and contained up to 73% of the energy from the input sludge.

Analytical results show that most of the heavy metals from the sludge are concentrated in the char and remain in the ash residual when the char is burned. Burning the oil and char as fuel will generate gaseous pollutants from sulfur and nitrogen in the sludge which could be a problem in commercial versions of the process.

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DIRECT THERMOCHEMICAL CONVERSION OF SEWAGE SLUDGE TO FUEL OIL, P.M. Molton, A.G. Fassbender, and M.D. Brown, Battelle, Pacific Northwest Laboratories, Richland, WA 99352.

An alternative disposal method for primary sewage and industrial sludges, which generates boiler fuel as a product and is energy self-sufficient or energy-generating, is described. The method involves direct liquefaction in mild aqueous alkali above 250 °C. The process has been successfully demonstrated in a prototype 12 gallon continuous reactor operated for 100 hr. The chemical liquefaction process converted 20% solids primary sewage sludge in high yield to a water-insoluble oil, a char, water-soluble organics, and gas. The oil and char were separable from the aqueous phase by gravity, in up to 73% energy yield based on input sludge energy. This is sufficient to fuel the liquefaction process, leaving up to 45% of the input energy as a surplus for in-plant generation of steam and electricity.

Analytical results show that the wastewater is highly treatable by conventional methods, and that the off-gas is primarily carbon dioxide. Inorganic heavy metals are concentrated into the char ash fraction. Burning the oil and char as fuel will generate gaseous pollutants from sulfur and nitrogen in the sludge, which could be a problem in commercial versions of the process. Mixing the feed with municipal solid waste is a possible solution to this problem. Preliminary cost analysis indicates that the liquefaction process should be competitive with incineration for cities over 1 million population.

DIRECT THERMOCHEMICAL CONVERSION OF SEWAGE SLUDGE TO FUEL OIL

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INTRODUCTION

The liquefaction process to be described here is not new, per se, but its application to the energy-efficient conversion of sewage sludge is at least novel. Variants on this process are in pilot plant or pre-pilot plant stage in several places in the world for the conversion of municipal garbage, wood wastes, peat, and other materials of organic nature. We are unaware of any real thought about potential environmental problems relating to the conversion, except for some preliminary work on the potential carcinogenicity of wood-derived oils (1), which is not strictly a pollution problem. This paper is directed towards a discussion of the liquefaction process for sewage sludge conversion and the potential for pollution if the process becomes practiced on a large scale. It represents an extension of our previous batch-scale conversion work to a continuous scale (2). Figure 1 shows a photograph of the reactor system, with the heated and pressurized reactor vessel (with white insulation) on the right.

Direct Thermochemical Liquefaction (DTL) is an aqueous hydrolytic degradation of organic materials to water soluble products, followed (in the same reactor) by a re-condensation to higher molecular weight materials including phenols, ketones, hydrocarbons, alicyclic compounds, and heteroaromatics such as furans, thiophenes, and pyrroles. Work performed at the Pacific Northwest Laboratory for the Department of Energy over the past several years (3-6) has helped us to elucidate the chemistry of the process in some detail. DTL is to be distinguished from pyrolysis, hydrogenation and other reductive conversions, fermentation, etc., on the basis of this chemistry. Results obtained on these other methods will probably not be directly transferable to DTL.

In the DTL conversion, primary sewage sludge or other organic material (excluding coal, oil, and some plastics) is slurried with water to about 20% solids and mixed with approximately 5% by weight of sodium carbonate. The mixture is heated in a pressure vessel to about 300 °C for a period exceeding an hour and then cooled, whereupon organic products separate spontaneously from the water phase and can be decanted or solvent-extracted. For a commercial application, we do not consider solvent extraction to be either environmentally desirable or economically feasible. The oil product from sludge liquefaction has a high energy content and can be used to fuel the process, in some cases with enough energy left over to provide steam or electrical generating

capacity. In a properly designed plant, energy breakeven becomes the baseline case, rather than something to be achieved with difficulty, as with some incinerators.

Depending on the reaction conditions, product separation from the wastewater may be anything from almost total to zero (an emulsion). In any case, reactor off-gas and wastewater represent potential pollution sources.

EXPERIMENTAL

Primary settled sewage sludge was obtained from the City of Richland, WA, and delivered to our facility by truck; it was then mixed with 1% polymer and dewatered to approximately 20% solids by a Bird 6" continuous centrifuge. The centrifuged material was then thoroughly mixed with 5% by weight of anhydrous sodium carbonate by continuously pumping it through a progressive cavity pump in the recirculation mode for 10 min. This highly alkaline mixture (pH about 11.6) was stable against bacterial action for several weeks.

Liquefaction of the raw material was performed in a prototype continuous reactor comprising a metering injection pump, injector, electrically heated reactor vessel, two pressure let-down vessels for liquid products, and a gas storage vessel for by-product gas. The reactor vessel was a 15 centimeter outside diameter vertical stirred tube, 3 meters in height, with the top and bottom thirds continuously scraped during operation. Sludge slurry injection was performed by filling the injector with the sludge feedstock and then pumping water through the injection pump at the required rate, causing displacement of the feedstock into the reactor vessel. The sludge and water were separated by a nylon piston. This arrangement avoided problems with direct pumping of sludge containing abrasive particles of grit and sand. As soon as the reactor was one third full of feedstock, heating was commenced using 13 KW ceramic radiative heating to the reactor wall, heat transfer to the interior of the sludge being enhanced by means of the scraper blades. Internal gas pressure was controlled with a sequence of back-pressure valves using nitrogen; excess gas was collected in the gas storage vessel. Periodically, when one of the pressure let-down vessels was full of liquid products, it was sealed off from the reactor and blown down into a 55 gallon drum.

The reactor was run for a total of almost 100 hr. under various conditions, ranging from a temperature of 250-315 ^{o}C, and a residence time for sludge in the reactor between 1.5 - 3 hr. The products were collected separately from each run and analyzed by various means, together with gas and feed samples. Internal conditions in the reactor were continuously monitored and recorded (on a floppy disc) through a series of thermocouples and pressure monitors connected to a data logger.

In addition to the large-scale continuous experiments performed as described above, several small-scale experiments were performed in a 180 ml Autoclave Engineers rocking autoclave using selected toxic chemical environmental contaminants as feedstocks. These experiments were performed to determine the ability of the DTL liquefaction method to destroy such chemicals when present in contaminated sludges.

Products consisted of gas, solid, and liquid materials. They were separated prior to analysis as follows: Gas produced during liquefaction and collected in the storage vessel was sampled and analyzed by gas chromatography (GC). Raw data were normalized by factoring out nitrogen and oxygen (diluent and contaminant, respectively). Wastewater, oil, and char were separated for analytical purposes by dichloromethane extraction of the homogeneous sample, followed by filtration, decantation of the solvent/oil lower layer, and evaporation under reduced pressure. Sludge feedstock samples were dried at 110 °C for 24 hr. prior to analysis.

Analytical determinations consisted of ultimate elemental analysis for C,H,N, and O using a Perkin Elmer elemental analyzer (model 240); X-ray fluorescence analysis for S,P, metals and trace elements using a variety of sources (7); water content of product oil was determined with a Photovolt Corp. Aquatest IV Karl-Fischer apparatus while water content of solids was determined by oven-drying at 110 °C for 24 hr. Ash content was determined after heating at 750 °C for 8 hr. Heat content of oil and char products was determined in a Parr bomb calorimeter according to ASTM D-3286-77. GC-Mass spectrometry was performed on a Hewlett-Packard model 5990 instrument.

Wastewater samples were filtered and dichloromethane extracted to obtain insolubles and solvent-soluble material concentrations, respectively; 5-Day BOD and COD were determined by standard methods using a seed from the City of Richland for BOD, and the dichromate oxidation method for COD. Total dissolved material was determined after evaporation under vacuum at 110 °C. for 24 hr.

RESULTS

Conversion of sewage sludge to other organic products was essentially total under all of the continuous reactor conditions used. Table I shows the relevant data for bulk characterization of the feed and products to demonstrate this point. Heat contents were increased in the product oil by a factor of over 2.5 over the feedstock. Char heat contents were lower because of the retention of most of the feed inorganic material in this product, but after correction for an average of 60 % ash, char heat contents were comparable to those of the oil. Table II presents the ultimate elemental compositions of the feedstock and the oil and char products. Carbon and hydrogen contents of the oil and char are both increased relative to the feed sludge, while oxygen content is considerably reduced.

Table I. Bulk properties of feed and products.

Property: / Material:	Temp. Conditions °C/min.	Yield, wt. % (a)	Ash %	Water, %	Heat, cal/g. (b)
Sludge feed	-/-	-	34.61	79.4	3202
Oil 208	305/90	10.2	7.4	8.36	8347
Oil 305	275/180	20.2	5.7	9.73	7802
Oil 306	305/180	24.9	6.3	5.16	8585
Oil 313	275/90	16.9	3.4	8.43	8692
Oil 418	275/90	17.6	0.5	5.54	8812
Char 208 (c)	305/90	23.6	59.0	-0-	2405
Char 305	275/180	11.3	79.1	-0-	1186
Char 306	305/180	15.0	78.1	-0-	1768
Char 313	275/90	12.0	56.9	-0-	3168
Char 418	275/90	24.1	50.2	-0-	2831

(a) Yield, wt. % was obtained by expressing the ratio of oil or char weight to that of input sludge weight in the same total weight of aqueous sample, as a percentage.
(b) Heat contents not corrected for ash and water in oil.
(c) Char was oven-dried prior to determinations.

The concentrations of some of the more pollution-generating elements (Cr, Cu, Zn, Pb, Cd, and Ba) are shown in Table III for feed and products (mercury is not shown because of interference by germanium).

Off-gas composition and wastewater analysis are shown in Tables IV and V, respectively. Table VI presents preliminary results from small-scale treatment of toxic organic pollutants by the DTL process in a small batch autoclave.

CONCLUSIONS

The DTL process is intended as an alternative to incineration. As such it must be competitive in terms of efficiency, economics, and low pollution levels. The work reported here deals with research; the DTL process for conversion of sewage sludge to fuel is not yet ready for commercialization. Hence, data on pollution levels are sparse. However, the results obtained to date with

Table II. Elemental composition of feed and products.

Element (a,b) Material:	C %	H %	O %	N %	Cl %	S %	P %
Feed sludge	51.68	7.38	42.13	2.41	0.10	0.71	0.90
Oil 208	76.17	10.25	9.30	1.99	0.07	0.59	0.05
Oil 305	71.27	9.77	10.83	3.89	0.19	0.86	0.10
Oil 306	70.63	9.92	9.43	2.57	2.22	0.63	0.04
Oil 313	73.31	10.24	10.94	3.01	0.02	0.58	0.06
Oil 418	74.76	10.20	8.71	2.82	0.06	0.99	0.05
Char 208	76.61	9.02	24.07	2.24	0.07	0.91	3.13
Char 305	60.09	7.49	56.46	5.01	0.06	0.96	3.85
Char 306	59.81	7.31	74.93	-0-	0.04	0.84	3.96
Char 313	72.72	9.20	54.66	3.45	0.08	1.06	2.26
Char 418	54.38	7.36	43.63	0.50	0.14	0.53	0.99

(a) Normalized, ash-free basis.
(b) Average of 2 values for C,H,O,N; average of 6 values for sludge feed. Oxygen determined directly, not by difference. Cl, S, P determined by X-ray fluorescence.
(c) Anomalous result probably due to ash inclusion.

Table III. Toxic inorganic elements. (a)

Element: Material:	Cr	Cu	Zn	Pb	Cd	Ba
Sludge 306	541	309	616	58.8	3.2	369
Sludge 418	103	339	651	53.7	5.0	319
Sludge 502-1	98	302	662	52.4	2.8	309
Oil 306	19.5	15.3	44	2.0	3.6	14.1
Oil 418	13.9	6.6	59	0.9	4.7	13.1
Oil 502-1	11.7	6.3	17	2.1	2.3	5.7
Char 306	1107	2100	2500	322	15.2	1900
Char 418	220	785	1347	157	7.0	520

(a) All values in ppm.

Table IV. Normalized reactor off-gas composition.

	Gas, %					
	Hydrogen	Carbon monoxide	Carbon dioxide	Ethylene	Ethane	Methane
Run #:						
208	10.45	0.08	86.74	0.53	0.48	1.76
305	19.94	-0-	75.05	2.30	2.23	0.69
306	17.03	-0-	79.62	1.53	1.59	0.56
313	-0-	-0-	98.26	1.33	-0-	0.68
418	-0-	0.57	98.40	0.33	-0-	0.31

Note: "Hydrogen" refers to free hydrogen gas.

Table V. Properties of wastewater.

Run #	COD	BOD	BOD/COD, %	TDS	Organics in TDS, %
305	52.6	40.2	76.4	ND	ND
313	61.8	37.9	61.3	ND	ND
418	ND	ND	ND	77.8	42.6
502-2	40.9	27.7	67.7	67.1	33.0
507-4	ND	ND	ND	77.0	40.

Values in g/l. BOD as glucose/glutamine equivalent. TDS = Total Dissolved Solids. ND = Not Determined (only representative wastewater samples were analyzed, rather than every sample).

the prototype continuous reactor are so encouraging in terms of process efficiency that we feel that the process is certainly economically viable and should compete well with incineration. If further research demonstrates that the DTL process has a high likelihood for pollution and would require much expensive clean-up equipment, then the economic picture may change, as it has done for other processes such as municipal solid waste pyrolysis, for example.

Table VI. Destruction of chlorinated organic compounds.

Compound	Conc., %	Temp., °C	% Remaining
Chloroform	0.8	290	-0-
Lindane, 25% mixed isomers	0.8	290	0.001
2,4,5-Trichloro-phenylpropionic acid	0.8	290	90
2,4,5-Trichloro-phenylpropionic acid	0.08	350	80

As we currently envision a commercial application of the process, primary sewage sludge from the settler would be dewatered by existing technology to a concentration between 20-40% solids. The thick slurry would then be mixed with alkali and pumped into the liquefaction reactor, where it would be heated to about 300 °C for approximately 30 min. Off-gas from the reactor during the conversion of the sewage sludge to products consists primarily of carbon dioxide and hydrogen, and could be disposed of by passing it through the reactor heat generation system. This would also involve the combustion of some volatile organic compounds entrained in the off-gas, although these would be small in amount. The reactor effluent, after pressure-let-down, spontaneously separates into an upper oil layer, a lower char layer containing varying amounts of adsorbed oil, and an intermediate clear brown water layer. The oil layer would be physically decanted or skimmed off, and the char layer dewatered by mild centrifugation and further dried in the exhaust gas from the heat generation system. Oil and char would then be recombined and burned in a high pressure steam boiler to generate heat for the reactor and for ancillary applications such as belt presses, centrifuges, etc. Wastewater would be recycled to the primary settler, after which it would pass through the conventional wastewater treatment system, where it would be readily biodegraded. (The wastewater from this process is typical of wastewaters from sludge thermal treatment processes in that it is heavily loaded with organics. Our calculations show that, starting with a 20% solids feed, process wastewater should not produce a significant increase in organic loading due to the high volume of primary wastewater going directly to the digestor). Although we used solvent extraction for separation of

analytical samples, we do not envision any use of solvents in a commercial version of the DTL process.

As described above, the input to the DTL reactor would be dewatered primary sewage sludge, and the effluent would consist of water, inorganic ash, and oil/char combustion products only. No additional fuel would be employed. This represents a major cost saving over incineration, but also means that the combustion gases from the boiler would not be diluted by carbon dioxide from burning clean fuel. As reference to Table II shows, the sulfur and nitrogen content of the oil and char is quite high, and could present a pollution problem. One way around this would be to mix the oil produced from sewage with normal boiler fuel, and use the sewage products as a supplement only. The problem here is that this may lead to an excess of energy availability over and above that required for use in the sewage treatment plant. A somewhat better possibility lies in the potential for co-conversion of sewage and municipal solid waste (MSW). The DTL process operates equally well for MSW or for sewage, or for that matter for any organic material including wood and peat, but excluding coal, plastics and petroleum. Mixing MSW with sewage would serve the purposes of MSW disposal, sewage water content reduction, and production of a cleaner-burning fuel due to the lower sulfur and nitrogen contents of the MSW.

One of the critical factors in evaluating the DTL process is its energy efficiency. A simple way to estimate this is to compare the heat contents of the feedstock with those of the products. An engineering estimate of energy requirements for liquefaction and product recovery can then be made, with certain assumptions for heat recovery included. From this basis a crude cost estimate for sludge disposal follows. In our pre-pilot plant work, the energy recovery from dry feedstock to dry products was in the range of 45-73%, using different liquefaction conditions. Assuming that the higher value can be duplicated on a larger scale, and bearing in mind that a primarily aqueous feed is converted to a water-immiscible product with very little energy input, we estimate that up to half of the chemical energy in the sludge feed could be available after reactor energy needs are satisfied. This estimate is heavily dependent on the efficiency of heat recovery and therefore on the size of the reactor system. For a small town of about 10,000 people, the use of sewage alone as a feedstock, and with essentially no heat recovery economically possible, sewage disposal capital costs are about $700/dry ton (Table VII). If heat recovery is practised, as for example in a town of 100,000 size, using a Dowtherm system, the unit cost drops to $113, and for a larger city of 1 million using a high pressure steam boiler, to $43/dry ton. This is predicated on the use of a 20% solids feedstock. Higher solids throughput, possible by dewatering to 40% solids or by mixing in MSW, would cause a major reduction in these costs.

Table VII. Preliminary DTL capital cost.

City size: Cost element: (in $x1000)	10,000	0.1 M	1.0 M
Design	100	200	500
Materials	470	1031	4466
Labor	75	250	1000
Management	25	40	150
Start-up materials	7	10	200
CAPITAL COST	670	1521	6316

To our knowledge, these are the first results reported on the liquefaction, as opposed to the pyrolysis or incineration, of sewage sludge in a continuous system. Pyrolysis generally requires a dry feedstock, as does incineration, except where external fuel is used to evaporate water in situ. Research still is required on the separation of products from DTL and on the distribution of pollutants resulting from liquefaction, both those originally in the sludge and those produced during liquefaction and the subsequent combustion of products. Nevertheless, we feel that DTL represents a promising alternative to more conventional methods in that it has the potential to generate more fuel than it uses for sludge disposal, in an environmentally acceptable manner.

Table VIII. Preliminary DTL operating cost.

City size: Cost element: ($x1000)	10,000	0.1 M	1.0 M
Debt, 8%/20 yr.	68	155	623
Maint. labor, supplies	25	25	100
Operator labor	40	80	250
Fuel, soda ash	15	100	750
Misc. supplies	25	25	100
Ann. oper. cost	173	385	1823
Ann. oper. revenue	-0-	56	557
Net annual cost	173	329	1266
Wt. sludge processed (dry tonnes/day)	0.8	80	800
SLUDGE DISPOSAL COST ($/dry ton)	593	113	43

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DISCLAIMER

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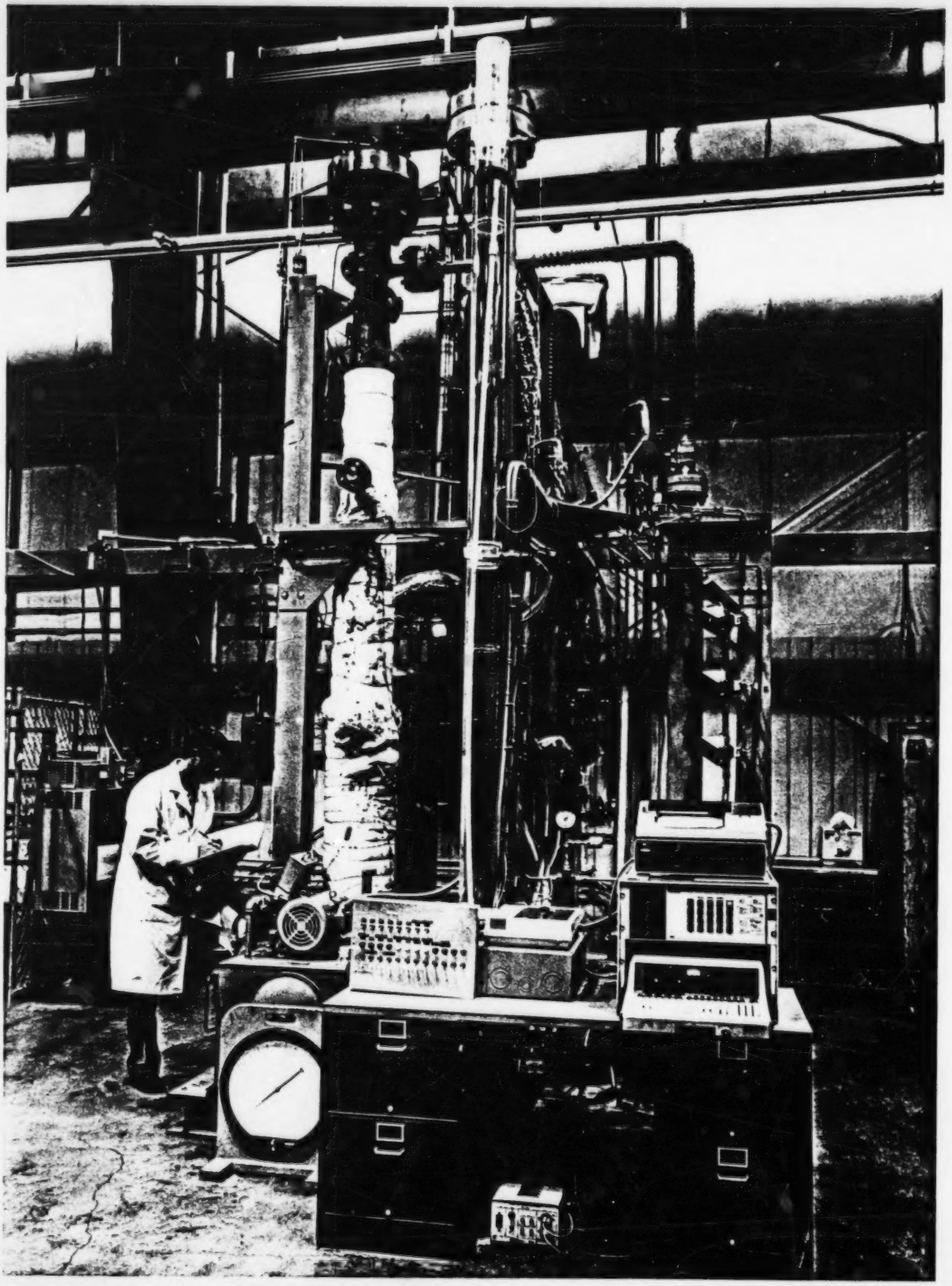

Figure 1: Sludge to Oil Reactor System.